

Corrosion of Pharmaceutical Equipment

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INTRODUCTION

Corrosion, the degradation of a material's properties or mass over time because of environmental effects, is a costly reality that effects every industry. A study issued by the Federal Highway Administration (FHWA) in 2002 conservatively estimates the annual direct cost of corrosion in all U.S. industry sectors at US\$276 billion. Costs associated with corrosion include cathodic/anodic protection; coatings; inhibitors; corrosion-resistant alloys and materials; and maintenance, repair, and depreciation of equipment. Indirect costs, such as lost productivity, environmental or product contamination, planning and design, and lost opportunities, can easily outpace direct costs by factors of two or more.

It is relatively easy to recognize the impact that corrosion has on chemical process industries (CPI). The FHWA indicates that annual direct costs for the refinery, chemical, petrochemical, paper, and food processing industries total US\$13.5 billion. In the chemical and pharmaceutical sector alone, the conservative estimate given is that corrosion costs are roughly 8% of capital expenditures. The US\$1.7 billion figure for this sector is very conservative because it does not include operating and maintenance costs. Corrosion within these industries ranges from mild (exposure of structures to atmospherical conditions) to very severe (strong acids, high temperatures, and halogen environments). Additionally, these industries use large quantities of water for not only chemical process, but for heating and cooling. The properties of water, a very mild corrodent, make it conducive to the electrochemical nature of corrosion processes. Acceptable performance of corrosion-resistant materials or systems can range from tens of years to weeks.

The control of corrosion in pharmaceutical product processes is largely managed through the use of stainless steel. Rust-free surfaces and cleanliness issues to prevent product contamination have been the primary corrosion concerns. Resistance to mildly aggressive cleaning solutions and saline solutions and the potential for under deposit or crevice corrosion present the most severe service conditions. The high standards of cleanliness necessary for pharmaceutical processes favor the mitigation of corrosion.

CORROSION BASICS

The broadest definition of corrosion is the degradation of a material's properties or mass over time because of the effect of the environment. We can think of this in simpler terms by recognizing this process as the tendency for a material to return to its most thermodynamically stable state. For most metallic materials, this means the formation of oxides or sulfides, or other basic metallic compounds generally considered to be ores. For polymeric materials, the end result could be a variety of simple organic compounds. Only in vacuums or under inert atmospheres can corrosion processes be expected to halt entirely. In most cases, these processes are slow enough to afford useful and practical equipment life.

Corrosion is an electrochemical process and corrosion processes follow the basic laws of thermodynamics. Under controlled conditions, corrosion can be measured, repeated, and predicted. However, because corrosion takes place on an atomic level, corrosion can take place in an accelerated localized fashion, appear as uniform visible attack, or result in subsurface microscopical damage. Normal service environments can rapidly complicate these processes and mechanisms with such variables as pH, temperature, stress, surface finish, flow rates, etc. With the wide range of variables that can come into play, it should not be surprising that corrosion appears to be unpredictable at times.

FORMS OF CORROSION

Corrosion of metallic materials can take on many forms. Understanding and recognizing the basic forms of corrosion are necessary for developing a strategy for mitigation. These concepts can also be utilized in assessing nonmetallic materials. Fig. 1 illustrates these basic corrosion mechanisms.

Uniform Corrosion

The simplest form of corrosion is "uniform" or "general" corrosion. This mode of corrosion is characterized by a uniform metal loss over the entire exposed surface. It is the most predictable and measurable form of corrosion.



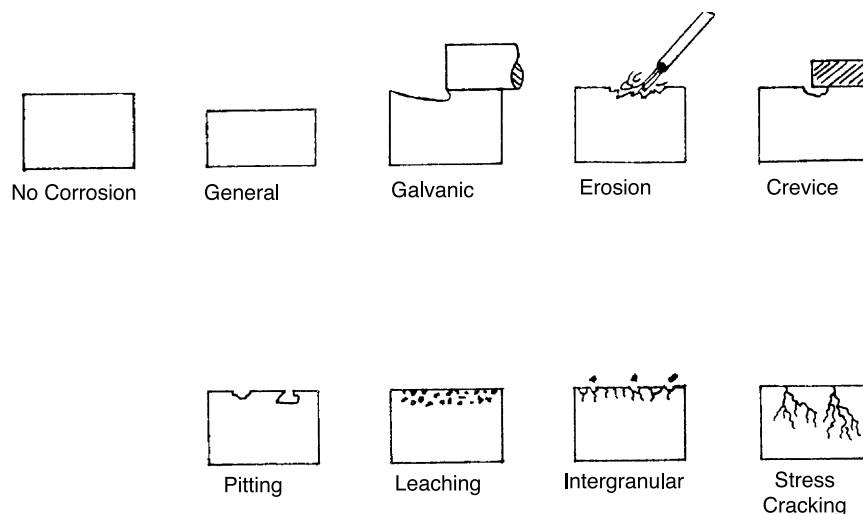


Fig. 1 Forms of corrosion.

There are many sources of general corrosion data that list actual or typical rates of corrosion for many materials in common environments. Where data are not available, simple laboratory tests can be conducted to simulate process environments.

The most common way to report uniform corrosion is in terms of metal thickness loss per unit of time, such as inches per year or millimeters per year. Because uniform corrosion is predictable, even moderately high corrosion rates can be tolerated provided a suitable monitoring and inspection system is utilized. For most chemical process systems, general corrosion rates of less than 2 mils per year (MPY) are acceptable. Rates between 2 and 20 MPY (1 mil = 0.001 in.) are routinely accepted as useful engineering materials. In severe environments, rates between 20 and 50 MPY may be economically justified. Rates exceeding 50 MPY are generally not acceptable.

For pharmaceutical applications in particular, the rate of corrosion must be considered not only for the effect on equipment, but where the lost metal has gone. Product contamination can be of concern for other products as well, and when this is an issue, the selection of more corrosion-resistant materials is of utmost importance.

Galvanic Corrosion

When two different metallic materials are electrically connected and placed in a conductive solution, an electrical potential will exist. This potential difference will provide a stronger driving force for the dissolution of the less noble (more electrically negative) material. It will also reduce the tendency for the more noble material to dissolve.

Although the relative differences in potential will change from one environment to another, they remain fundamentally the same because the potential is related to the energy required to oxidize them to metal ions in the given environment. The precious metals of gold and platinum are at the high potential (more noble or cathodic) end of the series, whereas zinc and magnesium are at the low potential (less noble or anodic) end. A galvanic series for a variety of metals in seawater is shown in Table 1.

Erosion Corrosion

Erosion corrosion results in an increased rate of corrosion attack attributable to the velocity of a corrodent over the exposed surface. The movement of the corrodent can be

Table 1 Galvanic series in seawater

Least Noble	Magnesium	
	Beryllium	
	Aluminum	
	Cadmium	
	Low Alloy Steel	
	Aluminum Bronze	
	Copper	
	Admiralty Brass	
	Martensitic Stainless	
	90-10 Copper-Nickel	
	Ferritic Stainless	
	70-30 Copper-Nickel	
	Nickel Alloy 200	
	Austenitic Stainless	
	Titanium	
	Superaustenitic Stainless	
Most Noble	Platinum	

When Active

associated with mechanical wear. The increased corrosion is usually related to the removal or damage of a protective surface film. The mechanism is usually identified by localized corrosion, which exhibits a pattern that follows the flow of the corrodent.

Fretting corrosion is a specialized form of erosion corrosion where two metal surfaces are in contact and experience very slight relative motion that causes damage to one or both surfaces. Again, in the presence of a corrodent, the movement causes mechanical damage of the protective film, leading to localized corrosion.

A second form of erosion corrosion is the case of cavitation. A type of corrosion familiar to pump impellers, this form of attack is caused by the formation and collapse of tiny vapor bubbles near a metallic surface in the presence of a corrodent. The protective surface film is again damaged, in this case by the high pressures caused by the collapse of the bubbles.

Pitting Corrosion

Pitting corrosion is in itself a corrosion mechanism, but is also a form of corrosion often associated with other types of corrosion mechanisms. It is characterized by a highly localized loss of metal. In the extreme case, a pit can appear as deep, tiny hole in an otherwise unaffected surface.

The initiation of a pit is associated with the breakdown of the protective film on the metal surface. In cases where pit depths increase rapidly, the environment is usually such that no repair or repassivation of the protective layer can be accomplished. In situations where many shallow pits form, the environment is usually one where repassivation of the damaged film can be made, but initiation of new sites occurs on a regular basis.

The localized nature of pitting attack can be associated with component geometry, the mechanics of the corrosion process, compositional inhomogeneity, or imperfection within the material itself. The growth of pits, once initiated, is closely related to another corrosion mechanism, crevice corrosion.

Crevice Corrosion

Crevice corrosion occurs in some environments because the nature of the environment within the crevice becomes more aggressive over time. There is little movement of the corrodent within a crevice. Over time, small changes in chemistry because of minor localized corrosion may become magnified because the solution is not being replenished by the bulk solution.

As a result of a slow initial rate of the corrosion, the pH of the crevice environment may become more acidic, or detrimental ion species may concentrate. As a result of

the low-flow condition, the crevice region may become depleted of oxygen, or preclude the replacement of reacted inhibitors.

Selective Leaching

Selective leaching is the process whereby a specific element is removed from an alloy because of an electrochemical interaction with the environment. Dezincification of brass alloys is the most familiar example of this type of corrosion. It occurs most commonly when there is exposure to soft waters and can be accelerated by high carbon dioxide concentrations and the presence of chloride ions.

The result of this corrosion is the formation of a porous and usually brittle shadow of the original component. Other alloy systems are susceptible to this form of corrosion. Examples include the selective loss of aluminum in aluminum–copper alloys, and the loss of iron in cast iron–carbon steels.

Intergranular Corrosion

As the name suggests, this particular corrosion mechanism attacks those sites where individual grains within a metallic material touch each other. These boundaries are natural regions of higher energy because of the greater frequency of dislocations of atoms from the natural order of the material's structure. In addition, these regions also tend to act as sites for the formation of secondary phases, which are essentially small islands within the matrix that have a chemical composition different from the alloy itself.

Depending on the corrodent and the alloy system, corrosion attack may initiate at these locations because of preferential attack of the secondary phase itself, or attack the surrounding matrix, which was locally dealloyed in forming the secondary phase. Either mechanism will result in the metallic surface being etched along the grain boundaries. As the attack progresses, individual grains are separated from the matrix and the surface layer becomes porous. In severe cases, the surface texture becomes grainy or powdery, leading to more rapid metal loss.

Stress Corrosion Cracking

The mechanism of stress corrosion cracking (SCC) is specific to certain alloys (or alloy systems) in specific environments. It is characterized by one or more crack fronts, which have developed as a result of a combination of the particular corrodent and tensile stresses.

Depending on the alloy system and corrodent combination, the cracking can be either intergranular or transgranular. The rate of crack propagation can vary greatly



and is affected by stress levels, temperature, and the concentration of the corrodent. In some severe combinations, such as type 304 stainless steel in a boiling magnesium chloride solution, extensive cracking can be generated in a matter of hours. In most industrial applications, the progress of SCC is, fortunately, at a much slower pace. However, because of the nature of the cracking, it is difficult to detect until extensive corrosion has already developed, which can lead to unexpected catastrophic failure. Alloy system and corrodent combinations that are known to exhibit SCC are fairly well documented and should be considered in initial design stages.

Apart from the SCC mechanism, stress can assist in other corrosion processes. Because this stress-assisted corrosion is related to tensile stresses, it is logical to expect that it will also accelerate the simple mechanical fatigue process. Corrosion fatigue is often difficult to differentiate from simple mechanical fatigue, but is recognized as a factor when the environment has been judged to have accelerated the normal fatigue process. Such systems can also have the effect of lowering the endurance limit such that fatigue will take place at a stress level wherein, without the environmental effect, fatigue failures would not be expected.

CORROSION MONITORING

The most common method of identifying and monitoring corrosion is visual inspection. Evidence of leakage, staining, or a change in surface appearance can be an indication that some type of corrosion is taking place. Experience with certain types of equipment and processes may help dictate inspection intervals and areas on which to focus the inspection. Records of vessel operation, maintenance, and repair can be helpful in establishing a pattern of performance that will improve predictability and minimize down time.

In areas where general corrosion is the expected form, a simple ultrasonic thickness gage can be utilized to determine the extent of corrosion, based on baseline readings made at installation or previous inspections. The entire unit need not be examined. Attention can be focused on those areas most likely to corrode, such as liquid levels, mixing zones, or areas of high turbulence. Corrosion probes, which can be placed in process equipment or pipelines, can monitor corrosion conditions by measuring an actual corrosion current, or other process parameters known to be related to general corrosion rates. These data can be constantly monitored and recorded to predict equipment wear, or as an alert to upset conditions.

For detection of more localized corrosion, such as crevice corrosion or SCC, other ultrasonic inspection

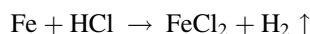
techniques may be useful. Baseline data generated at the time of installation will also be helpful in evaluating results. One benefit derived from this type of inspection technique is that it can often be conducted with little or no interference with production. Periodic planned visual inspection of equipment utilized under conditions likely to cause stress cracking is also an effective technique, especially when combined with nondestructive inspection techniques such as dye penetrant inspection. It may be necessary to remove coatings or insulation from the equipment surface to facilitate inspection.

CORROSION PROCESSES AND MITIGATION

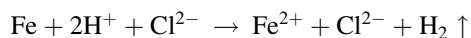
Electrochemical Nature of Corrosion

Corrosion, in its simplest definition, is the process of a material returning to the natural thermodynamic state. For most metallic materials, this means the formation of the oxides or sulfides that existed before being refined into useful engineering materials.

These changes are electrochemical reactions that follow the laws of thermodynamics. This concept aids in understanding why corrosion processes are time-dependent and temperature-dependent, and its application will indicate ways to mitigate corrosion. Corrosion reactions and rates are affected by ion and corrodent concentrations. One of the most basic corrosion reactions involves the oxidation of a pure metal when exposed to a strong acid. A familiar case is that of placing pure iron in hydrochloric acid. The resulting chemical reaction is quite obvious, with the solution beginning to bubble violently. The chemical reaction can be expressed as follows:



The result of this reaction is evidenced by the gradual disappearance of the iron and the hydrogen bubbles rising rapidly to the surface. On an electrochemical level, there is also an exchange of electrons taking place:



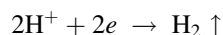
The iron has been converted to an iron ion by giving up two electrons (oxidation), which were picked up by the hydrogen ions. By gaining electrons, the hydrogen ion was *reduced* and formed hydrogen gas. Note that the chlorine atom does not enter into the reaction itself. The transfer of electrons takes place on the metal's surface. Those locations where electrons are being given up are identified as "anodes." The sites where electrons are being absorbed are denoted as "cathodes." A difference in electrical potential exists between these two areas and

a complete electrical circuit is developed. Negatively charged electrons flow in the direction of anode to cathode, and positively charged hydrogen ions in the solution move toward the cathode to complete the circuit. The faster the dissolution of the metal (rate of corrosion) is, the higher is the current flow. On a microscopical level, the sites of the anodes and cathodes can change locations on the surface. In fact, this is exactly what happens when general corrosion takes place, with the anodic areas moving uniformly over the metal's surface.

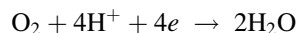
Anodic reactions in metallic corrosion are relatively simple. The reactions are always such that the metal is oxidized to a higher valence state. During general corrosion, this will result in the formation of metallic ions of all the alloying elements. Metals that are capable of exhibiting multiple valence states may go through several stages of oxidation during the corrosion process.

Cathodic reactions are more difficult to predict, but can be categorized into one of five different types of reduction reactions:

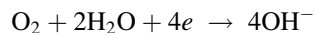
Hydrogen evolution



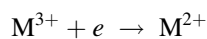
Oxygen reduction in acids



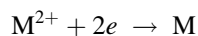
Oxygen reduction–neutral solutions



Metal ion reduction



Metal Deposition



Cell Potentials

Understanding electrochemical behavior and the possible reactions can help in predicting the possibility and extent of corrosion. A reaction will only occur if there is a negative free energy change (ΔG). For electrochemical reactions, the free energy change is calculated from:

$$\Delta G = -nFE$$

where n is the number of electrons, F is Faraday's constant, and E is the cell potential.

Therefore for a given reaction to take place, the cell potential must be positive. The cell potential is taken as the difference between the two half-cell reactions, the

one at the cathode minus the one at the anode. The half-cell potential exists because of the difference in the neutral state compared to the oxidized state, such as Fe/Fe^{2+} ; or, at the cathode, the difference between the neutral state and the reduced state, as in H^+/H_2 . These reduction–oxidation (redox) potentials are measured relative to a standard half-cell potential. The chart shown in Table 2 lists potentials relative to the H^+/H_2 , which is set as zero.

The larger this potential difference is, the greater is the driving force for the reaction. Whether corrosion does occur, and at what rate, is dependent on other factors. For corrosion to occur, there must be a current flow and a completed circuit, which is then governed by Ohm's law: $I = E/R$. The cell potential calculated here represents the peak value for the case of two independent reactions. If the resistance were infinite, the cell potential would remain as calculated but there would be no corrosion at all. The resistance in the circuit is dependent on a number of factors, including the resistivity of the media, surface films, and the metal itself. As current begins to flow, the potentials of both half-cell reactions move slightly toward each other. This change in potential is called polarization.

Once the corrosion current has been determined, the corrosion current density can be calculated by determining the surface area. However, polarization data can be more useful than just estimating corrosion rates. The extent of polarization can help predict the type and the severity of corrosion. As polarization increases, corrosion decreases. Polarization may be preferential to either the cathodic or anodic reactions. Understanding the influence of environmental changes on polarization can offer insights to controlling corrosion. For example, in the iron–hydro-

Table 2 Standard oxidation–reduction potentials

25°C, volts vs. hydrogen electrode	
$\text{Au} \leftrightarrow \text{Au}^{3+} + 3e$	1.498
$\text{O}_2 + 4\text{H}^+ + 4e \leftrightarrow 2\text{H}_2\text{O}$	1.229
$\text{Pt} \leftrightarrow \text{Pt}^{2+} + 2e$	1.2
$\text{Ag} \leftrightarrow \text{Ag}^+ + e$	0.799
$\text{Fe}^{3+} + e \leftrightarrow \text{Fe}^{2+}$	0.771
$\text{O}_2 + 2\text{H}_2\text{O} + 4e \leftrightarrow 4\text{OH}^-$	0.401
$\text{Cu} \leftrightarrow \text{Cu}^{2+} + 2e$	0.337
$2\text{H}^+ + 2e \leftrightarrow \text{H}_2$	0.000
$\text{Ni} \leftrightarrow \text{Ni}^{2+} + 2e$	−0.250
$\text{Fe} \leftrightarrow \text{Fe}^{2+} + 2e$	−0.440
$\text{Cr} \leftrightarrow \text{Cr}^{3+} + 3e$	−0.744
$\text{Zn} \leftrightarrow \text{Zn}^{2+} + 2e$	−0.763
$\text{Al} \leftrightarrow \text{Al}^{3+} + 3e$	−1.662
$\text{Mg} \leftrightarrow \text{Mg}^{2+} + 2e$	−2.363

Source: A. J. de Bethune and N. A. S. Loud, Standard Aqueous Electrode Potentials and Temperature Coefficients at 25°C, Clifford A. Hampel, Skokie, IL, 1964.



chloric acid example, hydrogen gas formation at the cathode can actually slow the reaction (increased circuit resistance) by blocking the access of hydrogen ions to the cathode site. This results in cathodic polarization and lowers the current flow and corrosion rate. If oxygen is bubbled through the solution, the hydrogen will be removed more rapidly by combining to form water and the corrosion rate increases significantly. Although this is an oversimplified view of the effects of oxygen, it does indicate that the degree of polarization can be affected by changes in the environment, either natural or induced.

Polarization

There are three basic causes of polarization. They are termed activation, concentration, and potential drop. Potential drop is the change in voltage associated with effects of the environment and the circuit between the anode and cathode sites. It includes the effects of the resistivity of the media, surface films, corrosion products, etc.

Activation polarization is because of a rate-controlling step within the corrosion reaction(s) at either the cathode or anode sites. An example of this can be seen with the H^+/H_2 conversion reaction. The first step of this process, $2H^+ + 2e^- \rightarrow 2H$, takes place at a rapid pace. The second part of this reaction, $2H \rightarrow H_2$, occurs more slowly and can become a rate-controlling factor.

Concentration polarization is the effect resulting from the excess of a species, which impedes the corrosion process, or from the depletion of a species critical to the progression of the corrosion process. The earlier case with an excess concentration of hydrogen gas impeding the rate of reaction is an example of concentration polarization. Although, in this case, it occurred at the cathode, it can also develop at the anode.

Measuring Polarization

Although polarization always leads to lower rates of corrosion, identifying the effects of the environment on polarization of the corrosion circuit is useful in predicting corrosion behavior. It is possible to measure the corrosion current while the corrosion potential is varied.

Most often, it is the anodic polarization behavior that is useful in understanding alloy systems in various environments. Anodic polarization tests can be conducted with relatively simple equipment and the scans themselves can be done in a short period of time. They are extremely useful in studying the active-passive behavior that many materials exhibit. As the name suggests, these materials can exhibit both a highly corrosion-resistant behavior or that of a material that corrodes actively, while in the same corrodent. Metals that commonly exhibit this type of

behavior include iron, titanium, aluminum, chromium, and nickel. Alloys of these materials are also subject to this type of behavior.

Active-passive behavior is dependent on the material-corrodent combination and is a function of the anodic or cathodic polarization effects, which occur in that specific combination. In most situations where active-passive behavior occurs, there is a thin layer at the metal surface that is more resistant to the environment than the underlying metal. In stainless steels, this layer is composed of various chromium and/or nickel oxides, which exhibit substantially different electrochemical characteristics than the underlying alloy. If this resistant, or passive, layer is damaged while in an aggressive environment, active corrosion of the freshly exposed surface will occur. The damage to this layer can be either mechanical or electrochemical in nature.

The behavior of iron in nitric acid underscores the importance of recognizing the nature of passivity. Iron is resistant to corrosion in nitric acid at concentrations around 70%. Once passivated under these conditions, it can also exhibit low rates of corrosion as the nitric acid is diluted. However, if this passive film is disturbed, rapid corrosion will begin and repassivation is not possible until the nitric acid concentration is raised to a sufficient level.

Anodic Polarization

Active-passive behavior is schematically represented by the anodic polarization curve shown in Fig. 2. Starting at the base of the plot, the curve starts out with a gradually increasing current as expected. However, at point A, there is a dramatic polarizing effect, which drops the current to a point where corrosion is essentially halted. As the

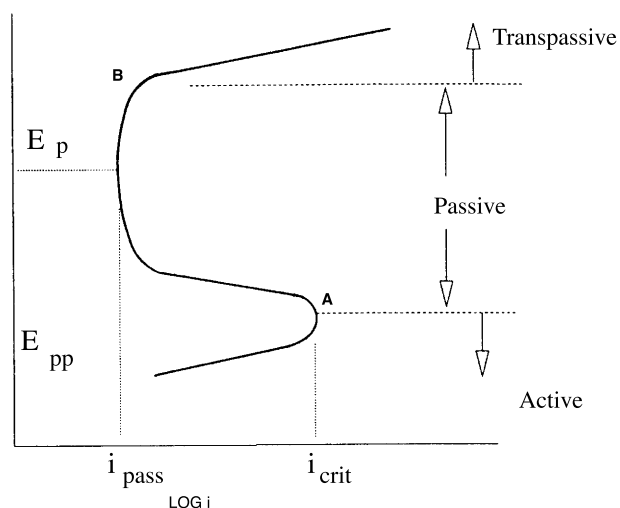


Fig. 2 Anodic polarization curve for a material exhibiting active-passive behavior.

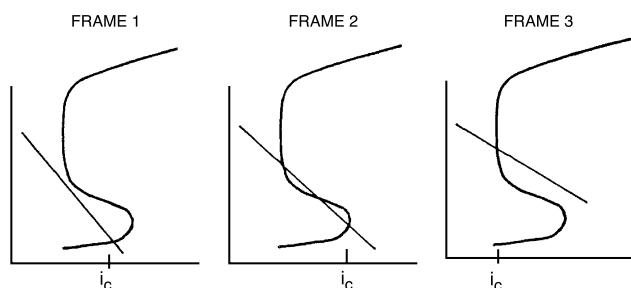


Fig. 3 Conditions within the corrosive environment can alter the cathodic polarization curve to create fluctuations between passive and active behavior.

potential is increased further, there is little change in current flow until the next critical stage, point B, where a breakdown of the passive film occurs, and the corrosion current again begins to rise.

Even with an established anodic polarization behavior, the performance of a material can vary greatly with relatively minor changes in the corrodent. This is also illustrated in Fig. 3. Frame 1 illustrates the case where the anodic and cathodic polarization curves intersect much as in materials with no active-passive behavior. The anode is actively corroding at a high, but predictable, rate.

Frame 2 represents the condition often found perplexing when using materials that exhibit active-passive behavior. With relatively minor changes within the system, the corrosion current could be very low as when the material is in the passive state, or very high when active corrosion begins.

Frame 3 typifies the condition sought after when using materials in the passive state. In this example, the cathodic polarization curve intersects only in the passive region, resulting in a stable and low corrosion current. This type of system can tolerate moderate upset conditions without the onset of accelerated corrosion.

CORROSION MITIGATION

The basic principles outlined here can be applied to identified corrosion problems and can provide solutions or alternatives. Corrosion control in many forms and approaches is founded on these concepts.

The principle of cathodic or “sacrificial” protection is founded in the natural potential differentials between different metals. Zinc anodes are intentionally placed in electrical contact with steel structures so that, as they corrode, the steel is protected. In other systems, a current may be applied to the structure to be protected so as to cause the current to flow to an artificial anode.

For similar reasons, it is desirable to build process systems out of the same materials. In systems where contact of dissimilar metals cannot be avoided, it is helpful to have the less noble material possess the largest surface area. By doing so, the corrosion current that is generated is distributed over a much greater area and slows the overall rate of penetration. In many such systems, it is also possible to electrically insulate one alloy network from the other.

Anodic protection finds its basis in the understanding of active-passive behavior. By increasing the potential of the component to be protected, it moves from an actively corroding situation to one where passivity can be induced. Such techniques can be quite cost-effective, but must be applied under well-controlled operating conditions because slight overprotection or underprotection can lead to accelerated rates of corrosion.

The types and varieties of inhibition systems are quite diverse, but also derive their fundamental logic from the principles reviewed here. Inhibitors slow corrosion by increasing polarization at either the anodic or cathodic reactions, or by increasing the electrical resistance of the media.

As an alternative to controlling the corrosion processes, the environmental conditions under which the system is operating may lend themselves to control. Temperature can have a significant influence on the corrosion process. This is not surprising because it is an electrochemical reaction and reaction rates do increase with increasing temperature.

If reducing the temperature is not possible, then it may be possible to eliminate one or more corrodents present, which are not critical to the product process. Halogen ions can be particularly aggressive on many materials and are often present only as a contaminant. Careful control of the pH can also be employed in many processes. There are additional environmental influences on corrosion other than the corrodent itself.

The relative velocities between the component and the media can have a direct effect on the corrosion rate. In some instances, increasing the velocity of the corrodent over the surface of the metal will increase the corrosion rate. When concentration polarization occurs, the increased velocity of the media will disperse the concentrating species. However, with passive materials, increasing the velocity can actually result in lower corrosion rates.

The surface finish of the component also has an impact on the mode and severity of the corrosion that can occur. Rough surfaces or tight crevices can facilitate the formation of concentration cells. Surface cleanliness can also be an issue with deposits or films acting as initiation sites. Biological growths can behave as deposits, or can change the underlying surface chemistry to promote corrosion.

One of the most common and cost-effective methods of preventing harmful corrosion is the selection of more



corrosion-resistant materials. In addition to selecting the proper material, fabricating and finishing the equipment can have critical impact on performance. Variations within the metal surface on a microscopical level influence the corrosion process. Microstructural differences such as secondary phases or grain orientation will affect the way corrosion manifests itself. For corrosive environments where grain boundaries are attacked, the grain size of the material plays a significant role in how rapidly the material's properties deteriorate. Chemistry variations in the matrix of weld deposits are also factors that must be considered in some corrosive environments.

The corrosion engineer can play a major role in system design, material selection, process or environmental control, and remediation. The focus of these efforts should not necessarily be the complete elimination or avoidance of corrosion, but rather the selection of the most cost-effective means of corrosion control and abatement.

MATERIAL SELECTION

The range and the availability of various types of engineering materials of construction continue to grow. As these materials improve, the benefits appear not only in terms of equipment reliability, but also processes pushed to more extreme conditions. These materials of construction can be generally classified as ferrous metals, nonferrous metals, plastics, elastomers, and other nonmetallics.

Ferrous Metals

This group of materials encompasses some of the most widely used construction materials as it includes steels and stainless steels. In pharmaceutical process applications, low-alloy steels are typically limited to structural uses and see little contact with product. Mild steels have been utilized successfully in stills, provided the oxygen content is maintained at very low levels. Tool and die steels may be used in areas where the product is dry and no corrosion is anticipated.

Steel and Stainless Steel

In areas where steels are in contact with the product or raw materials, stainless steels are often used as the workhorse. The production of stainless steel began in the early 1900s. The original efforts in this area were presumably based on the observation that chromium-plated steels parts were highly corrosion-resistant. The end result was the introduction of the ferritic *family* of stainless steels. The first documentation of the development of this class of steel began to appear in the 1920s. The first American Society

for Testing and Materials (ASTM) Specifications for stainless steels were published in 1935.

Today, there are seven basic families of stainless steels with compositions that contain 11–33% chromium, 0–38% nickel, and 0–7% molybdenum as the major alloying elements. These families are:

- Ferritic
- Austenitic
- Precipitation Hardenable
- Superferritic
- Martensitic
- Duplex (Ferritic-austenitic)
- Superaustenitic

Chromium is a metal that readily forms an oxide, which is transparent and happens to be extremely resistant to further degradation. As a further benefit to alloying with steel, it is less noble than iron and thus tends to form its oxide first. For exposure to mild, wet environments, the addition of about 11% chromium is sufficient to prevent “rusting” of steel components, hence the term “stainless.”

Ferritic stainless steels are magnetic, have body-centered cubic atomic structures, and possess mechanical properties similar to carbon steel, although less ductile. These materials are historically known as “400” series stainless as they were identified with numbers beginning with 400 when the American Institute for Iron and Steel (AISI) had the authority to designate alloy compositions. Alloy identification is now formally handled by the Unified Numbering System (UNS), where stainless alloy identification numbers generally begin with “S” followed by a five-digit number. Ferritic stainless steels find little application in the pharmaceutical industry owing to their low level of corrosion resistance and strength.

The corrosion resistance of the martensitic steels is again dependent solely on chromium, and because the carbon contents are generally higher than the ferritic alloys, they are less corrosion-resistant. Nevertheless, the combination of useful corrosion resistance in mild environments coupled with high strengths makes the martensitic stainless alloys candidates for cutting tools, molds, gears, shafts, and ball bearings.

Austenitic Stainless Steels

This family of stainless accounts for the widest usage of all the stainless steels. These materials are nonmagnetic, have face-centered cubic structures, and possess mechanical properties similar to the mild steels, but with better formability. The AISI designation system identified the most common of these alloys with numbers beginning with 300 and resulted in the term *300 series* stainless. Table 3 lists the chemical analyses of some standard

Table 3 Typical chemical compositions of some common stainless and nickel alloys

Alloy	Family	C	Cr	Ni	Mo	N	Nb	Other
430	Ferritic	0.07	16.5	—	—	—	—	
304 L	Austenitic	0.025	18.2	8.6	—	0.04	—	
316 L	Austenitic	0.025	16.5	10.5	2.2	0.04	—	
410	Martensitic	0.1	12.0	—	—	—	—	
17-4 PH	Precipitation-hardenable	0.04	16.2	4.2	—	—	0.25	3.6 Cu
Alloy 20	Superaustenitic	0.02	19.5	33.0	2.2	—	0.5	3.2 Cu
AL-6XN [®]	Superaustenitic	0.02	20.5	25.0	6.1	0.22	—	
Sea-Cure [®]	Superferritic	0.02	26.0	2.5	3.0	0.025	0.3	0.3 Ti
2205	Duplex	0.02	23.0	5.5	3.0	0.18	—	
C-276	Nickel alloy	0.01	16.0	57.0	16.0	—	—	3.5 W
625	Nickel alloy	0.02	22.0	61.0	8.9	—	3.6	0.25 Ti

AL-6XN is a registered trademark of Allegheny Ludlum.

Sea-Cure is a registered trademark of Colt Industries.

austenitic stainless steels and compares them to a few materials from other families of materials.

Once the corrosion resistance plateau in ferritic alloys of 18% chromium is reached, the addition of about 8% nickel is required to cause a transition from ferritic to austenitic. The primary benefit of this alloy addition is to achieve the austenitic structure, which, relative to the ferritics, is very tough, formable, and weldable. The added benefit, of course, is the improved corrosion resistance to mild corrodents. This includes adequate resistance to most foods, a wide range of organic chemicals, mild inorganic chemicals, and most natural environmental corrosion.

Nickel is used judiciously as an alloying element because its cost is substantially higher than chromium. However, type 304 is balanced near the austenite–ferrite boundary for another reason. Compositions similar to type 304 that are unable to form ferrite when solidifying after welding are prone to cracking during solidification and are more difficult to hot work. As a result, adding more nickel to the 18–8 composition offers little benefit from a corrosion standpoint and would be detrimental in other regards.

The next major step in alloying additions comes from molybdenum. This element also provides excellent corrosion resistance in oxidizing environments, particularly in aqueous corrosion. It participates in strengthening the passive film, which forms on the stainless steel surface along with chromium and nickel. A significant benefit is realized with the addition of only about 2% molybdenum. Added directly to the 18–8 composition, the alloy would contain too much ferrite so it must be rebalanced. The resulting chemistry is roughly 16% chromium, 10% nickel, and 2% molybdenum, and is recognized as type 316 stainless.

Austenitic alloys also make use of the concept of stabilization. Stainless types 321 and 347 are versions of

type 304 stabilized with titanium and niobium, respectively. These elements will preferentially combine with carbon that comes out of solid solution during weld solidification. Rather than a loss of corrosion resistance associated with formation of harmful chromium carbides, the carbides of titanium and niobium are not detrimental to corrosion resistance. The austenitic family of stainless also prompted another approach to avoiding the effects of chromium carbide precipitation. Because the amount of chromium that precipitated was proportional to the carbon content, lowering the carbon could prevent sensitization. Maintaining the carbon content to below about 0.035% vs. the usual 0.08% maximum will avoid the precipitation of harmful levels of chromium carbide. This discovery, along with improvements in melting technology, resulted in the development of the low-carbon version of many of these alloys. When first introduced, Extra Low Carbon (ELC) grades (i.e., 304 L and 316 L) required premiums on pricing because of higher production costs. This differential has essentially disappeared in the face of modern argon–oxygen decarburization (AOD) furnaces.

Argon–oxygen decarburization furnaces, utilized as a final refining stage in melting, are designed to permit the bubbling of the molten steel with oxygen, which facilitates the removal of carbon and sulfur. During this process, the exposed surface of the melt is protected with an inert argon atmosphere. This arrangement also permits bubbling with nitrogen gas, which will dissolve as atomic nitrogen into the steel. Nitrogen acts in a fashion similar to carbon by pinning slip planes, thus leading to higher-strength materials.

Modern melting technology is also responsible for another trend in stainless metallurgy. At one time, the permissible chemistry ranges for alloying elements needed to be broad to accommodate inhomogeneity in electrical furnace melts, chemical analysis variations, and



Table 4 Typical mechanical properties of some common stainless and nickel alloys

Alloy	Condition	Tensile (KSI)	Yield (KSI)	Elongation (%)	Toughness (ft lb at °F)
430	Annealed	74	45	28	75 at RT
304 L	Annealed	75	28	55	80 at -300°
316 L	Annealed	75	28	55	110 at -300°
410	Full hard	188	155	17	49 at RT
17-4 PH	900° aged	198	183	15	16 at RT
Alloy 20	Annealed	90	48	45	145 at -300°
AL-6XN	Annealed	110	55	50	85 at -300°
Sea-Cure	Annealed	95	80	30	DBTT near -10°
2205	Annealed	98	70	25	80 at -40°
C-276	Annealed	110	55	50	240 at -40°
625	Annealed	120	65	50	35 at -320°

raw material quality. For example, the chromium range for type 304 was 8.0–10.0, and still heats were occasionally missed. With current technology, it is possible to maintain $\pm 3\sigma$ limits on chromium to 0.5% or better. The result is that alloys are currently being produced with 0.50–0.75% less of an alloying element than they were just 15 years ago.

Even with alloying additions such as molybdenum to improve localized corrosion resistance to halogens, the workhorse 304 L and 316 L alloys are susceptible to chloride SCC. This cracking mechanism manifests itself as branched, generally transgranular cracks that are so fine as to be virtually undetectable until it has progressed to catastrophic proportions. This mode of failure can occur when the austenitic alloy is under stress in the presence of halogen ions at temperatures above about 120°F. Studies by Copsen underscored the benefit of very low nickel contents, such as the ferritic stainless steels, or nickel levels in excess of about 20%. In fact, the nickel contents in these two alloys are in the range that tends to crack most quickly in chloride-bearing environments.

Duplex Stainless Steels

Stainless alloys that contain roughly equal amounts of austenite and ferrite are termed duplex stainless. This family of alloys grew out of one basic material originally identified as type 329. They are balanced to contain relatively high chromium contents, with only enough nickel and austenitizers to develop about 50% austenite.

These alloys offer several useful advantages. First, their general corrosion resistance is typically slightly above that of 316 L in most media. In addition, because the nickel content is held low, they offer very good resistance to chloride SCC. In combination with good corrosion resistance, duplex stainless alloys offer higher strengths than those typically found with austenitic steels.

Table 4 compares some typical mechanical properties for common stainless and nickel alloys.

Although more formable than the ferritic alloys, they are not as ductile as the austenitic family of alloys. Welding requires more care than with the austenitic alloys because of a greater tendency toward compositional segregation and sensitivity to weld heat input. Improper fabrication techniques can result in equipment that falls short of expectations for corrosion resistance and mechanical properties.

Superaustenitic

During the 1970s and into the 1980s, there was much attention focused on a family of stainless alloys, which came to be identified as superaustenitic. The foundation for the development of this class of materials was in the development of Carpenter no. 20 stainless, introduced in 1951. Consisting of 28% nickel and 19% chromium with additions of molybdenum and copper, this alloy was first produced as a cast material.

20Cb-3 Stainless became popular in the CPI as an intermediate step between type 316 stainless and the more highly alloyed nickel base materials. In particular, it was a cost-effective way to combat chloride SCC. Because of the high nickel content of 20Cb-3 Stainless, it received a nickel base alloy UNS designation as UNS N08020. However, because the major constituent is iron, it is truly a stainless steel. The superaustenitic term is derived from the fact this composition is so far from austenite–ferrite boundary that, unlike the 300 series stainless alloys, there is no chance of developing ferrite in this material.

The main approach to improving the pitting and crevice corrosion resistance of the basic 35% nickel, 19% chromium, and 2% molybdenum alloy was to increase the molybdenum content. Among the first of the newer alloys introduced was 904 L (UNS N08904), which boosted the molybdenum content to 4% and reduced the

nickel content to 25%. The reduction in nickel content was beneficial as a cost-saving factor, with minimal loss of general corrosion resistance and sufficient resistance to chloride SCC.

The next progression was to raise the molybdenum content to a higher level of 6% and to offset the tendency for the formation of sigma phase by the alloying addition of nitrogen. This concept was introduced with two alloys, 254SMO[®] (UNS S31254) and AL-6XN[®] (UNS N08367). The major benefit of the addition of nitrogen was the ability to produce these alloys in heavy product sections such as plate, bar, and forgings. An additional benefit was derived from alloying with nitrogen in terms of increased pitting resistance. A significant amount of work by a large body of researchers has demonstrated a relationship between pitting or crevice corrosion resistance and alloy content, which is approximated by:

$$\text{Cr}\% + 3.3*\text{Mo}\% + 16*\text{N}\%$$

where increasing values indicate increased resistance. A value in excess of approximately 33 is considered necessary for pitting and crevice resistance to ambient seawater.

Other Stainless

The precipitation-hardenable family of stainless alloys utilizes thermal treatment to intentionally precipitate phases, which cause a strengthening of the alloy. The precipitating phase is generated through an alloy addition of one or more of niobium, titanium, copper, molybdenum, or aluminum. The metallurgy is such that the material can be solution-treated (i.e., all alloying elements are in solid solution and the material is in its annealed or softest state). In this condition, the material can be machined, formed, and welded in the desired configuration. After fabrication, the unit is exposed to an elevated temperature cycle (aging), which precipitates the desired phases to cause an increase in mechanical properties.

As a class, these alloys offer high mechanical properties, although not as high as martensitic low-alloy steels, in combination with very useful corrosion resistance. On average, their general corrosion resistance is below that of type 304 stainless. The corrosion resistance of the PH 15-7 Mo and A-286 alloys approaches that of type 316. The martensitic and semiaustenitic pH grades are resistant to chloride cracking. These materials are susceptible to hydrogen embrittlement. In the pharmaceutical industry, these materials might find useful applications in valve components, bolting materials, or wear surfaces.

The ability of the ferritic alloys to resist chloride SCC is one of their most useful features in terms of corrosion resistance. During the 1970s, developmental efforts were directed at producing ferritic materials that could also

exhibit a high level of general and localized pitting resistance as well.

The first commercially significant alloy to meet this expectation was an alloy containing 26% chromium and 1% molybdenum. To obtain the desired corrosion resistance and acceptable fabrication characteristics, the material had to have very low interstitial element contents. To achieve these levels, the material was electron beam-refined under a vacuum, and was introduced as E-BRITE[®] Alloy. Carbon plus nitrogen contents were maintained at levels below 0.020%.

Materials such as SEA-CURE[®] (S43635) and 29-4C[®] Alloy (S44735) represent the most recent developments in superferritic materials. These alloys do exhibit excellent localized corrosion resistance. Although the superferritic materials alloyed with some nickel have improved mechanical toughness and are less sensitive to contamination from interstitial elements, their availability is still limited to heat exchanger tubing with wall thicknesses below about 0.100 in. This is related to the formation of embrittling phase during cooling from annealing temperatures. Section thicknesses over these levels cannot be cooled sufficiently fast to avoid a loss of toughness.

Cast Stainless Steel

The discussion thus far has been devoted to examining the different families of stainless steel metallurgy. The alloys discussed were wrought materials (i.e., materials that are hot-worked following being cast into ingots). The practice of hot working steels improves the uniformity of their chemical, mechanical, and corrosion-resistant properties. These materials are suited for fabrication by bending and welding.

Cast stainless steels can be divided into the same families as the wrought materials, except for the superferritics. Castings offer the particular advantage of being able to obtain complex shapes without extensive fabrication or machining. Cast alloys usually cost less per pound than the wrought counterpart because the hot working operations are avoided. Cast stainless steels can also have chemistry modifications to enhance properties that would otherwise render them unworkable as a wrought product. Heat-resistant cast alloys, such as HK, usually have high carbon and silicon contents, which improve elevated temperature strength considerably, but at the expense of room temperature toughness. The cast structure of such materials is also less resistant to thermal fatigue than the wrought material.

Although the compositions of the basic austenitic cast alloys are very similar to the wrought versions, the cast versions usually contain significant amounts of delta ferrite. As in the solidification of weld metal, ferrite is



beneficial in reducing the tendency for the material to form cracks during solidification. The ferrite content in CF-8M can approach 20% and can readily attract a magnet. Although high ferrite contents are often not of concern, the ferrite can be attacked preferentially in some environments such as urea, nitric acid, and hydrochloric acid.

The existence of significant amounts of ferrite is one form of segregation that can be encountered in cast stainless alloys. Because cooling rates are generally slow for cast components, other secondary phases can form. Chromium carbide precipitation is a particular concern for many of these materials and, under most circumstances, the casting should be solution-annealed prior to being placed in corrosive service.

NONFERROUS METALS

Nickel Alloys

Nickel is very effective in improving the corrosion resistance of stainless steels and is also utilized as the base material for a number of specialty alloys. By definition, nickel alloys contain more nickel than any other constituent. Alloy 625 has been widely used throughout the CPI for its corrosion resistance to strong acids, including hydrochloric acid, and for its resistance to halogen attack. This material also has excellent high-temperature mechanical properties and is used in gas turbine applications. Another nickel base alloy more familiar to the pharmaceutical industry is alloy C-276. This alloy combines the general corrosion resistance advantages of nickel with the benefits of oxidation and localized corrosion resistance derived from chromium and molybdenum.

Nickel alloys are also austenitic, nonmagnetic under all conditions, and possess formability similar to the austenitic stainless steels. The same welding techniques utilized for stainless alloys can be used for joining the nickel alloys.

Recent additions to the wide range of nickel alloys include materials designed to resist even more severe environments, such as hot halogenated acids, which are likely to induce crevice corrosion. Such materials include alloy 686, alloy 59, and alloy C-2000. These materials contain high levels of chromium (over 22%) and molybdenum (over 15%).

Other Nonferrous Materials

Other significant nonferrous materials include copper, aluminum, and titanium, and their alloys. Copper is resistant to most neutral waters, including seawater, and to strong reducing acids. However, it is not resistant to oxidizing acids, amines, metal salts, and sulfur compounds,

and is also sensitive to erosion from high velocities. Aluminum is useful in resisting atmospherical corrosion and neutral waters, but can corrode quickly in acids or bases. As such, copper and aluminum alloys are used sparingly in the CPI.

Titanium offers a much broader range of corrosion resistance and its applications are similar to those of the superaustenitic stainless steels and some nickel alloys. It has good resistance to pitting and crevice corrosion. Titanium alloys offer good general corrosion resistance to a variety of oxidizing and reducing acids. Although titanium alloys can be fabricated by welding, the required procedures are best suited for shops geared for this type of work. Field fabrication and repair are possible, but do require specialized equipment and procedures.

PLASTICS

This is a huge general category of materials, which includes both thermoplastics and thermosetting polymers. Tabular data on the corrosion resistance of these materials in a wide range of environments are available from a variety of sources. Commonly used materials of construction in the CPI include polyvinyl chloride (PVC and CPVC), polyethylene, polypropylene, polystyrene, polycarbonate, polytetrafluoroethylene (PTFE), fiberglass composite materials, and a variety of epoxies used for coatings or adhesives.

This class of materials can be a solution to handling a wide range of very aggressive chemicals, often resulting in a cost savings over more expensive metallic materials. However, some important differences between these materials and metals can limit their application. First, there is a maximum temperature limitation for these materials, which generally ranges from 120°F to 400°F. Many of these materials are limited to useful service temperatures below 200°F. Second, corrosion of these materials rarely occurs by direct material loss through a chemical reaction similar to that of metallic materials. The degradation of properties is usually the result of permeation by, or absorption of, the corrosive media. This attack can result in embrittlement, softening, blistering, crazing, swelling, dissolution, or some other loss of physical properties. Finally, the mechanical strength of this group of materials is generally lower than that of metal alloys. This can usually be accommodated through design, or with suitable exterior support structures.

Within the pharmaceutical industry, these materials are utilized for bulk acid storage at room temperature, storage of dry powders, piping of potable water, sewer lines, and wastewater treatment. The Food and Drug Administration (FDA) recognizes acceptable materials for food contact in the Code of Federal Regulations (CFR) 21 part 177.

ELASTOMERS

Elastomers or rubbers are also available in a wide variety of chemistries starting with natural rubber and including neoprene, urethane, polyester, silicone, and fluoroelastomers. These materials are subject to the same types of degradation as the thermoplastic materials. Temperature limitations are similar, or perhaps slightly lower.

The widest usage of these materials within the chemical process and pharmaceutical industries is for gasket and sealing applications, linings, flexible tubing, electrical insulation, and drive belts.

OTHER NONMETALLICS

Included in this category are materials such as concrete, chemical-resistant grouts, ceramics, and glass. These materials are highly resistant to chemical attack from most media normally encountered in the chemical process and pharmaceutical industries. In general, their usage is restricted as they tend to be brittle, have poor mechanical properties in tension, and are sensitive to thermal shock.

Chemical-resistant grouts and mortars and ceramic tile systems are very effective in providing cleanable surfaces, such as flooring and walls, and for containment. Ceramics are typically silicate-based materials, but there are also types produced from metallic oxides, nitrides, borides, and carbides. Although they generally have good corrosion resistance, they can be attacked by strong, hot alkalis and acidic fluoride media. The chemical-resistant grouts utilize inorganic binders, fillers, and a hardener. The exact formulation utilized must be based on the resistance to the environment to which it will be exposed.

Glassware and glass-lined equipment also offer excellent resistance to corrosion, similar to that of ceramic materials. In addition to the advantages of corrosion resistance, it also affords a very cleanable surface. Glass-lined vessels are used in the pharmaceutical industry for reactors, mixers, storage tanks, transfer piping, and high-purity water systems.

EQUIPMENT AND SERVICE CONSIDERATIONS

Welding

From an engineering standpoint, the ability to weld stainless steels with relative ease is a major advantage to their usefulness. Weld deposits, because they are cast structures, are subject to discussion regarding corrosion resistance similar to the cast materials. The chemistry of a weld deposit is likely to exhibit segregation and, depending on the alloy and the welding technique employed, may

develop deleterious secondary phases in either the weld or heat-affected zone.

Two ways to address this concern have already been discussed. These involve the reduction of carbon content to low levels and the use of stabilizers to prevent chromium depletion. Either of these methods is typically used for components that are assembled in the field, because subjecting the fabricated unit to an annealing treatment is neither practical or desirable in most instances.

In many cases, a small decrease in the corrosion resistance of weldments is tolerable. When the environment is particularly severe for the alloy being used, the weld may be attacked preferentially. This condition can be exaggerated by the area effects of the more noble base metal compared to the small weld zone. An alternate approach for field welding is to select a higher alloy welding consumable so the weld deposit is more noble than the base metal. Preferential attack can also occur in the heat-affected zone of the base metal. This is typical of weldments made in standard type 304 where the carbon content will lead to chromium carbide precipitation. Of course, this condition cannot be avoided by using a different filler metal and the only remedy is a postweld anneal.

Aside from the actual weld deposit chemistry, welding techniques can have an influence on corrosion resistance. First and foremost, the area to be joined should be clean and free of dirt and grease. Carbonaceous materials will contaminate the weld deposit and will deplete chromium from the alloy. For a similar reason, carbon arc gouging or cutting should be avoided. Contamination from other metals should also be avoided. Although free iron will essentially be melted into the weld deposit unnoticed, rust can affect weldability. At best, it can lead to lack of fusion or porosity and, at worst, it may act as a preferential site for the onset of corrosion. Joint preparation should be accomplished using properly sharpened tooling, and wire brushing should be performed using stainless steel brushes.

Low-melting-point metals are of particular concern. Molten copper, zinc, or aluminum will attack the grain boundaries of austenitic alloys preferentially. Copper alloy clamps or fixtures used to hold work, whereas welding has been known to leave smears of metal that have subsequently caused cracking. Zinc from galvanized steel or paint primers has also been known to contaminate weld joints.

Full-penetration weld joints should also be made. This is a good practice from a strength and fatigue resistance standpoint, but is also a factor in avoiding corrosion. Unfused joints are sites likely to trap corrosive products increasing the likelihood that oxygen or metal ion concentration cells are developed. This will generally mean that joints will have to be beveled if the thicknesses to be joined are in excess of 3/16 in. Beveling joints also insures that adequate filler metal will penetrate to the root in those instances where overalloying is desired.

Finally, the surface finish of the weld area should be similar to that of the base metal. Although a slightly higher roughness is usually unavoidable unless welding is followed by grinding to blend in the weld, minimizing roughness in the weld zone can be beneficial. Weld spatter should be removed by grinding. The weld slag from covered electrodes, which prevents oxidation of the metal during solidification, should be completely removed prior to making a second weld pass or placing the weld in service. Slag deposits on the surface will act as crevices in corrosive service. Removal of heat tints on the surface from bare wire or autogenous welding processes is preferred. In severe service, these areas may be attacked preferentially.

Passivation

Stainless steels offer useful resistance because they tend to exhibit passive corrosion behavior as a result of the formation of protective oxide films on the exposed surfaces. Under normal circumstances, stainless steels will readily form this protective layer immediately on exposure to oxygen. When this protective film is violated or fails to form, active corrosion can occur. Some fabrication processes can impede the reformation of this passive layer, and to insure that it is formed, stainless steels are subjected to "passivation" treatments.

The most common passivation treatments involve exposing the metal to an oxidizing acid. Nitric and nitric-hydrofluoric acid mixtures comprise the predominant usage in stainless steel production. The nitric-hydrofluoric acid mixtures are more aggressive and are typically used to remove the oxide scales formed during thermal treatment. This "pickling" process provides two benefits. First, it removes the oxide scale and passivates the underlying metal surface. Second, because of its aggressive nature, the process will remove any chromium-depleted layer that may have formed as a result of the scale formation.

For passivation treatments other than scale removal following thermal treatment, less aggressive acid solutions are usually employed. The primary purpose of these treatments is to remove contaminants that may be on the component's surface and could prevent the formation of the oxide layer locally. The most common contaminant is imbedded or free iron particle from forming or machining tools. Mechanical polishing can be employed to provide a uniform surface finish and to remove these contaminants. The polishing materials should be used for stainless only as they can carry over small particulates from one part to the next. In addition, the work-hardened state of this fine particulate, even from a stainless vessel, can have a lower threshold for corrosion and act as an initiation site if not removed. A dilute (10%) solution of nitric acid is effective at removing free iron, or similar contaminants. For ferritic, martensitic, or precipitation-hardening grades, a nit-

ric acid solution inhibited with sodium dichromate is used so as not to attack the stainless too aggressively. For the more resistant stainless alloys, phosphoric acid at 1% concentration and citric acid at 20% concentrations are also effective. Other commercially available chelating agents can be employed.

Electropolishing

Electropolishing is actually controlled corrosion, resulting in the uniform removal of the surface layer of metal. Electropolishing is not a passivation treatment, although the process does result in a passive surface. Proper electropolishing technique maintains the part in the electrochemically passive range whereas the passivated layer is only allowed to grow several atoms thick, at most. The electrolyte simultaneously promotes dissolution of this layer. The electropolishing process does remove surface impurities as is accomplished with passivation. During the cleaning and rinsing process following electropolishing, the material does passivate naturally on exposure to oxygen containing rinse water or air. No additional passivation procedure is required.

Electrolytes used for electropolishing are usually proprietary mixtures with contents that are not quantitatively revealed. Any electrolyte will typically have the ingredients to facilitate three different actions of the polishing process. These are: 1) a contaminant, which facilitates the breakdown of a passive film; 2) an oxidizer, which helps form a passivating film; and 3) a highly viscous constituent, which promotes the formation of a diffusion layer. The oxidizer and the contaminant assist in maintaining the part in a pseudo-passive state whereas the diffusion layer control is necessary to promote uniform metal loss. This is illustrated in the potentiodynamic graph shown in Fig. 4. For electropolishing 316 L stainless, the electrolyte will often contain perchloric acid, which can provide both oxidizing power and a halide contaminant. Acetic anhydride may be used to control the

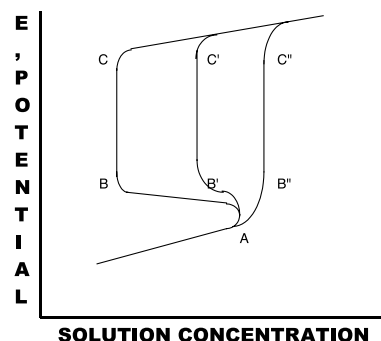


Fig. 4 Anodic polarization curve illustrating the unstable state created and maintained during electropolishing.

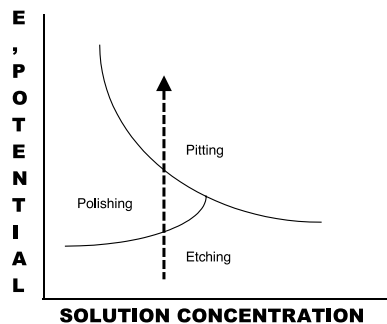


Fig. 5 Schematic diagram illustrating how, as electropolishing potential is increased, conditions may change from etching to polishing and, finally, to pitting.

diffusion layer. Stainless and higher nickel alloys might also use nitric acid, sulfuric acid, phosphoric acid, hydrogen peroxide, and methyl alcohol.

Determining the ideal electrolyte ingredients is an important part of the process. Because this is an electrochemical process, other variables to be controlled include the voltage, current density, and solution temperature. As illustrated in Fig. 5, voltages that are too low can cause etching of the surface because of more rapid general corrosion; too high a voltage will result in pitting. Cathode design is important because it is imperative to distribute the current as uniformly as possible over the part's surface.

Rouging

Rouging is a phenomenon of particular interest to the pharmaceutical industry. It is the presence of a surface layer of oxide found on stainless equipment or piping, typically handling high-purity water at temperatures above ambient. This includes stills, steam systems, purified water, and water for injection (WFI). The oxides can range in composition, degree of oxidation, color, texture, and adherence. Although generally shown to be innocuous, the mere presence of these deposits can raise concern.

The rouge itself is typically composed primarily of iron oxides or iron hydroxides, but because these are developing on stainless surfaces, they also contain oxides of chromium, nickel, and molybdenum as well. There are empirical data indicating that resistance to rouging increases with increasing Cr/Fe ratios in the passive layer, and/or the depth of the passive layer itself. Because electropolishing and passivation both increase the Cr/Fe ratio, application of these processes can increase resistance to rouging. Even with such treatments, the passive layer can break down because of the ionizing effect of high-purity water. The low oxygen content of these waters also slows the rate of repassivation and may cause the layer to linger in intermediate states of oxidation.

Repeated cycles of this process result in the entrapment of various oxides in the passive layer, hence the wide variation in colors.

Removal of rouging can be accomplished mechanically, but is usually addressed by chemical cleaning. Repassivation treatments with nitric, phosphoric, citric, or other oxidizing acid solutions have been effective in removing or fully reoxidizing this layer. As with any chemical reaction, the process is time-dependent and can be influenced by temperature. For more resistant rouge patterns, reducing acids such as hydrofluoric or hydrochloric may be used in combination with a passivation treatment. The use of these acids in strong concentrations may etch the surface.

Potentiodynamic polarization studies have been conducted to measure the efficacy of passivation treatments. It has been shown that the breakdown (pitting) potential is raised by passivation or electropolishing techniques, which result in higher Cr/Fe ratios and increased depth of the passive layer. These potentials can be increased by as much as 50–100 mV over mechanically polished or pickled surfaces, and have been equated to increased resistance to rouging. Additionally, breakdown potentials of the 6% molybdenum alloy N08367 were shown to be 400 mV higher prior to enhancing passivation treatments, and another 50 mV higher following such treatments. Such studies would suggest that higher alloys such as N08367 or the C-276 type alloy are highly resistant to rouging.

SUMMARY

This discussion provides for a fundamental understanding of corrosion and corrosion processes. It also offers an overview of both metallic and nonmetallic materials utilized in the construction of pharmaceutical equipment and some of the special considerations in their application. Suppliers of materials and fabrication services are valuable resources of information and should be included in the design process. Because corrosion processes are often complex, the services of corrosion engineering professionals should be considered in the original design or performance analysis activities as part of an in-house team, or on a consulting basis.

REFERENCES

1. Brasunas, A. *NACE Basic Corrosion Course*; National Association of Corrosion Engineers: Houston, TX, 1970.
2. Dillon, C. *Corrosion Control in the Chemical Process Industries*; Material Technologies Institute for the Chemical Process Industries: St. Louis, MO, 1994.

3. Darken, L.; Gurry, R. *Physical Chemistry of Metals*; McGraw-Hill: New York, NY, 1953.
4. Fontana, M.; Greene, N. *Corrosion Engineering*; McGraw-Hill: New York, NY, 1967.
5. Gonzalez, M. Materials of Construction for Biopharmaceutical Systems. In *ASME Bio Process Seminar, San Juan, PR*; January, 2003.
6. Grant, A. CIP and Passivation. In *ASME Bio Process Seminar, San Juan, PR*; January, 2003.
7. Henthorne, M. *Corrosion, Causes and Control*; Chemical Engineering Magazine: New York, NY, 1971–1972.
8. McGannon, H. *The Making, Shaping and Treating of Steel*; United States Steel Corporation: Pittsburgh, PA, 1971.
9. Sedriks, A. *Corrosion of Stainless Steels*; John Wiley and Sons: New York, NY, 1979.
10. Schweitzer, P. *Corrosion and Corrosion Protection Handbook*; Marcel Dekker: New York, NY, 1996.
11. West, J. *Electrodeposition and Corrosion Processes*; Van Nostrand-Reinhold: London, UK, 1971.
12. *20Cb-3 Stainless Steel*; Carpenter Technology Corporation: Reading, PA, 1987.
13. *AL-6XN Alloy*; Allegheny-Ludlum Corporation: Pittsburgh, PA, 1991.
14. *Corrosion Costs and Preventative Strategies in the United States, A Review by Materials Performance, MP Supplement*; July, 2002.
15. *Mechanical and Physical Properties of the Austenitic Chromium–Nickel Stainless Steels at Elevated Temperatures*; The International Nickel Company: New York, NY, 1963.
16. *Metals Handbook*, 10th Ed.; ASM International: Materials Park, OH, 1990.
17. *Steel Castings Handbook*; Steel Founder's Society of America: Rocky River, OH, 1981.

